



Monitoring and Laboratory Division  
Air Quality Surveillance Branch

**Protocol for the Ambient  
Air Monitoring of Propanil**

June 13, 2008

Prepared by:

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**Signatures:**

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Air Resources Board

The following protocol has been reviewed and approved by staff of the Air Resources Board (ARB). Approval of this protocol does not necessarily reflect the views and policies of the ARB, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

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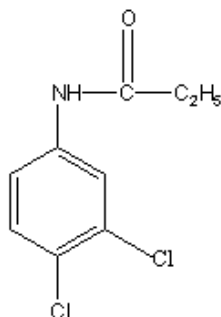
## 1.0 Introduction

At the request of the Department of Pesticide Regulation (DPR), January 4, 2008 Memorandum, Warmerdam to Goldstene of the the Air Resources Board (ARB) staff will determine airborne concentrations of Propanil in Colusa, Glenn and Butte Counties. Ambient air monitoring will be done over a eight (8) week period. This monitoring will be done to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5, Section 14022(c)) which requires the ARB "to document the level of airborne emissions.... of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. Monitoring is being conducted to coincide with the use of propanil as an herbicide used exclusively on rice and is a high priority for risk assessment.

The draft "Standard Operating Procedure Sampling and Analysis of S-methyl-N((methylcarbamoyl)oxy)thioacetamidate (Methomyl)" dated June 2007, is included as Appendix A.

## 2.0 Chemical Properties of Propanil

Figure1. Chemical structure of Propanil



Propanil is a colorless odorless crystal which breaks down rapidly in water due to sunlight. Table 1 lists physical-chemical properties of propanil. The low vapor pressure indicates that the potential to become vapor when applied is low. However, drift of propanil during peak use periods is a problem.

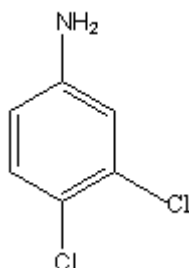
Chemical name	propanil
Trade names†	Duet, Propanil 4, Riceshot, Stam , Wham, Super Wham
CAS Registry number	709-98-8
Molecular formula	C <sub>9</sub> H <sub>9</sub> Cl <sub>2</sub> NO
Molecular weight	218.1 g/mol
Melting point	91.5 °C
Vapor pressure	9 x 10 <sup>-5</sup> mm Hg (60 °C)
Specific gravity	1.41 g/cm <sup>3</sup> (22 °C)
Water solubility	0.13 g/l (25 °C)
Henry's Law Constant	4.5X10 <sup>-9</sup> atm-m <sup>3</sup> /mole at 25 °C
Soil particle adsorption	149 –220 (K <sub>OC</sub> )
Octanol / Water Partition Coefficient (log K <sub>OW</sub> )	3.3
Hydrolysis half-life a day	Short half-life in water; less than
Soil half-life	1-3 days (microbial degradation)

Table1.

Physical and chemical properties of propanil (Tomlin, (ed.) 1994., The Crop Protection Handbook 2005., EXTONET 1993., DPR, 2006 and Spectrum Chemical Fact Sheet).

† Disclaimer: The mention of commercial products, their sources, or their use in connection with material reported herein should not be considered as either an actual or implied endorsement of such products.

Figure 2 Chemical structure of 3,4-Dichloroaniline



3,4-Dichloroaniline is the major breakdown product of propanil. In rice plants propanil is rapidly hydrolyzed to yield free 3-4-Dichloroaniline, which binds to lignin in rice leaves.

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Chemical name	3,4-Dichloroaniline
CAS Registry number	95-76-1
Molecular formula	(C <sub>6</sub> H <sub>3</sub> )Cl <sub>2</sub> (NH <sub>2</sub> )
Molecular mass	162.0 g mol <sup>-1</sup>
Boiling point	272 °C
Melting point	72 °C
Vapor pressure	15.012 x 10 <sup>-3</sup> mm Hg (20°C)
Relative density	1.36 g cm <sup>3</sup> (water = 1)
Water solubility	92 mg/l at 20 °C
Henry's Law Constant	1.9 x 10 <sup>-6</sup> atm-m <sup>3</sup> /mole at 25 °C
Soil particle adsorption	bound to soil 80% K <sub>OC</sub> 239 (sand)-800 (silt loam)
Field dissipation half-life	in soil 1.5 days
Octanol / Water Partition Coefficient (log K <sub>OW</sub> )	2.69

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Table 2

Propanil is a herbicide which is used against a variety of grasses and broad-leaved weeds in rice.

Thirteen propanil containing products are registered in California as of February 2008 (DPR, 2006). In rice, the maximum recommended dose per application is 6.0 lbs active ingredient (a.i.) per application per acre or 8.0 lbs a.i. per acre per season. This is a mitigation measure to reduce the likelihood of drift. Propanil is applied to target plants using ground equipment such as tractor-mounted sprayers or aerially. Both helicopters and fixed-wing aircrafts are used in aerial applications. Aerial applications using fixed-wing aircraft are considered most problematic. High frequency of aerial applications coupled with wind causes drifting.

As a post emergent herbicide on rice, it is recommended to apply on completely drained or fields with minimal standing water. Propanil should not be applied to standing water. It controls a variety of grassy weeds and sedges in young rice fields.

### **3.0 Project Goals and Objectives**

The goal is to measure the concentrations of propanil in ambient air in Colusa, Glenn and Butte Counties.

To achieve the project goals, the following objectives should be met:

1. Identification of monitoring sites that mutually satisfies criteria for ambient air sampling and DPR's requirements.
2. Appropriate application of sampling/monitoring equipment to determine ambient propanil concentrations.
3. Application of relevant field quality assurance/quality control practices to ensure the integrity of field samples.
4. At the conclusion of the project, MLD and results gathered in the course of MLD's activities during the planning will provide DPR with a final report containing all relevant information, data and execution of this project.

## 4.0 Contacts

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## 5.0 Study Location and Design

Propanil applications are performed throughout the Sacramento Valley. DPR has identified that June and July are when applications are at their peak.

### Ambient Air Monitoring

Ambient air monitoring for propanil will consist of six sampling sites (five air monitoring sites and one urban background site). The background samples will be collected at the Chico air monitoring station approximately 24 miles away from propanil use. There will be four (4) 24-hour samples per site each week. Sampling will be conducted during the peak months for 8 weeks from late May to July. In addition to the primary samples, replicate (co-located) samples will be conducted on four (4) dates at each sampling site. Field spike samples will be collected in the same environment. Target 24-hour quantitation limit of  $1.0 \text{ ug/m}^3$  for propanil is recommended by DPR. Sampling will also include a collocated sampler at each sampling site for the first four weeks.

A 47 mm quartz fiber filter will be placed on a Airmetrics MiniVol Portable sampler for 24 hours at a flow rate of 3.0 liters per minute (Lpm). The sampling flow rates of 3.0 Lpm for propanil will be accurately measured and the sampling system operated continuously for 24 hours with the exact operating interval recorded in the logbook. Each sampler inlet height will be 1.5 meters above roofline or in an open secured area which meets siting criteria for the ambient monitoring. At the end of each sampling period, the filters will be placed in a secure filter container with an identification label affixed. Subsequent to sampling, the sample filters will be transported in an ice chest, as soon as reasonably possible, to the ARB Sacramento Monitoring and Laboratory Division laboratory for analysis. The samples will be stored in the freezer or extracted/analyzed immediately.

Each sampler flow rate will be checked, using a mass flow meter (MFM), at the beginning and the end of each sample period. Samplers will be leak checked prior to each sampling period with the filter installed. Any change in the flow rates will be recorded in the field logbook. The field logbook will also be used to record start and stop times, start and stop flow rates, start and stop counter readings, sample identifications and any other significant data.

DPR supplied in their recommendations 16 communities based on propanil use and their Environmental Justice Rankings. A Geographic Information System was used to calculate the amounts of propanil used within 1 mile and 5 miles from the edge or boundary of each community using a buffering algorithm.



Propanil use in 2004-2006 and community environmental justice factors indicate that ambient air monitoring should occur over a 8-week period during June, July and August in Colusa, Glenn or Butte Counties.

The ambient monitoring sites chosen are located in the Colusa, Glenn, and Butte Counties. See the following:

Chico Air Monitoring Station (urban background site)  
468 Manzanita Avenue  
Chico, CA 95926  
530-949-7496

Public Works Office  
755 6<sup>th</sup> Street  
Williams, CA 95987  
530-473-2519

George T. Egling Middle School  
813 Webster Street  
Colusa, CA 95932  
530-458-8107

Maxwell Elementary School  
146 North Street  
Maxwell, CA 95955  
530-438-2401

Willows Intermediate School  
1145 W Cedar Street  
Willows, CA 95988  
530-330-1042

Richvale Elementary School  
5236 Church Street  
Richvale, CA 95974  
530-868-1281

## **6.0 Sampling and Analysis Procedures**

Special Purpose Monitoring Section (SPM) personnel will hand-carry samples to and from MLD's laboratory in Sacramento, and to and from the sampling location. The samples will not be exposed to extreme conditions or subjected to rough handling that might cause loss or degradation of sample.

At each sampling site, the operator will assure following each sampling period, the quartz filter will be placed in a secure filter container with an identification label affixed identifying the sample name and run date. The sample run information for each period will be recorded on the filter transfer sheet which will accompany the filters when delivered to the lab. Subsequent to sampling, the sample filters will be transported in an ice chest, as soon as reasonably possible, to the ARB Sacramento Monitoring and Laboratory Division laboratory for analysis. The samples will be stored in the freezer or extracted/analyzed immediately.

All reported sampling times will be reported in Pacific Standard Time (PST).

The Northern Laboratory Branch (NLB) will supply SPM with 47 mm quartz filters. NLB will perform analyses for propanil on collected ambient samples and report results to SPM.

Laboratory analyses will be performed in accordance to the Standard Operating Procedure for Sampling and Analysis of 3,4-Dichloropropionanilide (Propanil) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector. The SOP is included in this Protocol as Appendix A.

The following quartz fiber filter validation and analytical quality control criteria should be followed during pesticide analysis.

1. **Sample Hold Time:** Sample hold time criteria will be established by the Laboratory. Samples not analyzed within the established holding time will be invalidated by the Laboratory.
2. **Duplicate Analysis:** Laboratory to establish relative percent difference (RPD) criteria for duplicate analysis. Lab to provide duplicate analytical results and RPD.
3. **Method Detection Limit (MDL):** MDL sample analytical results less than the MDL shall be reported as a less than numerical value. This less than numerical value shall incorporate any dilutions/concentrations.
4. **Estimate Quality Limit (EQL):** This EQL reporting convention shall be eliminated. In the past, measurements falling between the MDL and five times the MDL (EQL) were reported as “detect”. All values at or above the MDL shall be reported as a numeric value.
5. **Analytical Linear Range:** Any analytical result greater than 10% of the highest calibration standard shall be reanalyzed within the calibrated linear range.

## 7.0 List of Field Equipment

<u>Quantity</u>	<u>Item Description</u>
(1)	Global Positioning System (GPS) with backup batteries and carrying case
(1)	Digital Camera with backup batteries and carrying case
(1)	Alborg mass flow meter 0-10 Lpm.
(13)	Mini-Vol samplers with chargers, batteries and filter holders
(12)	Tripod stands with hooks attached
(1)	Ladder
(6)	Extension cords



Figure 1  
Mini-Vol Air Sampler

## 8.0 Quality Control

Quality control procedures will be observed to ensure the integrity of samples collected in the field. National Institute of Standards and Technology (NIST)-traceable transfer standards will be used to calibrate meteorological sensors and measure sample flow rates.

The sample flow rate of the Airmetrics MiniVol portable sampler flow will be measured using mass flow meters having a current calibration certification and a flow range of 0-10 Lpm.

Each quartz fiber filter will be assigned a field sample number that provides for identification of site, sample ID number, operator, and sample information as well as sample transfer information.

**Field Spike (FS):** A field spike will be prepared by the laboratory by injecting a quartz fiber filter with XX ng/ml of propanil. The field spike is installed onto a sampler and will be colocated next to the background sampler. The ambient field spikes will be co-located at the background site.

**Trip Spike (TS):** A trip spike will be prepared by the laboratory by injecting a quartz fiber filter at the same level as the field spike. The trip spike will be transported and analyzed along with the field spike. The trip spike is treated the same as a field spike with exception that it is not installed onto a sampler.

**Trip Blank (TB):** A trip blank will be prepared by the laboratory. The trip blank quartz fiber filter accompanies the sample filters from the lab to the field and back but is not installed onto a sampler.

**Collocated (CO):** For ambient monitoring, colocated (side-by-side) air samplers will operate at each site, on four (4) separate days, throughout the monitoring period.

## **Site/Sample Identification**

The propanil sampling sites will be named accordingly for the locations, Date and type of sample:

### **Ambient Site Naming:**

CHIC 1-40	Chico Air Monitoring Station
IAMS 1-40	Public Works Office
MAXW 1-40	Maxwell Elementary School
WILL 1-40	Willows Intermediate School
COLU 1-40	George T. Egling Middle School
RICH 1-40	Richvale Elementary School

Note: Site addresses are located section 3.0 page 9

### **Letter Abbreviations as follows**

FS = Field Spike

CO= Co-located

TS = Trip Spike

TB = Trip Blank

## **9.0 Deliverables**

### **9.1 Air Quality Surveillance Branch Deliverables**

Within 90 days from receipt of the final results report from the Northern Laboratory Branch (NLB), AQSB will provide DPR with a report containing the following topics:

- 1) Sampling Protocol.
- 2) Personnel Contact List.
- 3) Site Maps.
- 4) Site Photographs.
- 5) Site Descriptions and Measurements, GPS coordinates inlet height.
- 6) A map of the monitoring site locations.
- 7) Sample Summary Table.
- 8 Field Sample Log.
- 9) Laboratory Analysis Reports with calculations in electronic format.
- 10) Transfer Standards' Certification Reports.
- 11) Disk containing electronic files of Report.

In addition, the Special Purpose Monitoring Section (SPM) will prepare a project binder containing the above information. This binder will remain with SPM though available for viewing and review as requested.

## **Northern Laboratory Branch (NLB) Deliverables**

Within 60 days from the last day of analysis, The NLB will provide SPM with a report that will include the following topics:

- 1) Table(s) of sample to include:
  - a. Sample identification (name).
  - b. Date sample received from field.
  - c. Date sample analyzed.
  - d. Dilution ratio.
  - e. Analytical results.
- 2) All equations used in calculating analytical results.
- 3) Table of duplicate results including calculated relative percent difference (RPD).
- 4) Table of collocated results.
- 5) Table of analytical results from all field, trip and laboratory spikes including percent recoveries.
- 6) Table of analytical results from all trip blanks.
- 7) Table of analytical results from all laboratory blanks, standards and control checks performed, including dates performed and relative percent recoveries if applicable.
- 8) Copy or location of analytical method or Standard Operating Procedures (SOP) used for analysis.
- 9) Section or provision listing or reporting any and all deviations from analytical SOP and this protocol.





## **APPENDIX A:**

### **Standard Operating Procedure Analyses for Propanil**

The Special Analysis Laboratory Section of MLD's Northern Laboratory Branch will perform the analyses for propanil collected by the quartz fiber filter method. Laboratory analyses will be performed in accordance with applicable standard operating procedures (Standard Operating Procedure for Sampling and Analysis of 3,4-Dichloropropionanilide (Propanil) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector).

**Standard Operating Procedure for Sampling and  
Analysis of 3,4-Dichloropropionanilide (Propanil)  
in Ambient and Application Air using Gas  
Chromatography/Mass Selective Detector**

**Special Analysis Section  
Northern Laboratory Branch  
Monitoring and Laboratory Division**

Revision 1  
8/01/08

Approved by:

Russell Grace, Manager  
Special Analysis Section

DISCLAIMER: Mention of any trade name or commercial product in this Standard Operating Procedure does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the Standard Operating Procedures are equipment used by the ARB laboratory. Any functionally equivalent instrumentation can be used.

## **1. SCOPE**

The current method is for the analysis of 3,4-dichloropropionanilide (Propanil) using a gas chromatograph/mass selective detector. The procedure is for the analysis of ambient and application air monitoring of propanil using quartz fiber filters. The Department of Pesticide Regulation (DPR) asked the Air Resources Board (ARB) to analyze for propanil during agricultural application and ambient monitoring with an estimated quantitation limit of 1.0 µg/m<sup>3</sup>.

## **2. SUMMARY OF METHOD**

Quartz fiber filters are placed on the ambient sampler for 24 hours at a flow rate of 3.0 liters per minute (LPM). Application sampling will vary from 2 hours to 24 hours. The samples are stored in an ice chest or refrigerator until extracted with 10.0 ml of dichloromethane (DCM). A gas chromatograph with a mass selective detector in the selected ion monitoring (SIM) mode is used for analysis.

## **3. INTERFERENCES/LIMITATIONS**

Interferences may be caused by contaminants in solvents, reagents, glassware and other processing apparatus that can lead to discrete artifacts or elevated baselines. A method blank, including both solvent and filter, must be analyzed with each batch of samples to detect any possible interference. Presence of a phthalate peak near the retention time of the propanil necessitates rinsing the filters for a minimum of 10 minutes in dichloromethane and air dry before use.

## **4. EQUIPMENT AND CONDITIONS**

### **A. INSTRUMENTATION:**

Hewlett-Packard 6890 Series gas chromatograph  
Hewlett-Packard 5973 Network mass selective detector  
Hewlett-Packard 6890 Enhanced Parameters ALS

MS Transfer line: 280°C

Injector: 250°C

Pulsed splitless: pulse pressure, 50.0 psi, pulse time 1.0 min. Purge flow 50.0 mL/min, purge time 0.95 min.

Liner 4 mm deactivated single taper gooseneck.

Column: J&W Scientific DB-5MS, 30 meter, 250 µm i.d., 0.25 µm film thickness, or equivalent

GC Temperature Program: Oven initial 110°C, hold 0 min. Ramp to 240°C @

12°C/min., ramp to 300°C @ 20°C/min., hold 1.0 min.

Retention time: Propanil 8.76 min.

Column Flow: He, 2.0 mL/min, 21.8 psi. (velocity: 53cm/sec)

Mass Spectrometer: Electron Ionization

Selective Ion Monitoring: propanil: 161 (quant. ion 100%), 163 (qual. ion 62%); Tuning: PFTBA on masses 69, 219, 502

#### B. Auxiliary Apparatus

1. Precleaned amber vials, 12 mL capacity with teflon caps
2. Pipettors, 10 mL capacity; Pasteur pipettes.
3. Sonicator.
4. GC vials with septum caps.
5. Filter holders, 47 mm and transport containers, BGI Waltham, Mass.

#### C. Reagents

1. Dichloromethane, Pesticide grade or better
2. 3,4-Dichloropropionanilide (Propanil), Chem Service PS-356, 99.0%
3. Whatman Quartz fiber filters QM-A, 47 mm, rinsed and dried.

### 5. ANALYSIS OF SAMPLES

1. A daily manual tune shall be performed using PFTBA. The instrument is tuned using masses: 69, 219, 502. The criterion for the tune are the peak widths at  $\frac{1}{2}$  the peak height,  $0.60 \pm 0.05$ , and the criteria for relative abundance: 69:100%, 219:90-120%, and 502: 5-12%.
2. It is necessary to analyze a solvent blank with each batch of samples. The blank must be free of interferences. A solvent blank must be analyzed after any sample that may result in possible carry-over contamination.
3. A five-point calibration curve shall be analyzed with each batch of samples. The calibration will be 0.01-0.20  $\mu\text{g/mL}$  for ambient studies and 0.40-4.0  $\mu\text{g/mL}$  for application.
4. A calibration check sample (0.05  $\mu\text{g/mL}$  or 0.5  $\mu\text{g/mL}$ ) is run after the calibration, after every ten samples and at the end of the sample batch. The value of the calibration check must be within  $\pm 3\sigma$  (the standard deviation) or  $\pm 10\%$  of the expected value whichever is greater. If the calibration check is outside this limit, then those samples in the batch after this calibration check need to be reanalyzed.
5. With each batch of samples analyzed, a laboratory (filter) blank and a laboratory (filter) control spike will be run concurrently. A laboratory blank is a filter extracted and analyzed the same way as the samples. A laboratory control spike is a filter spiked with a known amount of

standard. The laboratory control sample is extracted and analyzed the same way as the samples. Laboratory control samples should have recoveries that are greater than or equal to 70% of the theoretical spiked value.

6. Remove the filter from the holder, transfer into a 12-mL vial. Add 10.0 mL of DCM into the extraction vial. Cap and let the vial sit for one hour.
7. Transfer the sample directly into a GC vial and cap securely. The remainder is placed in the refrigerator.
8. The atmospheric concentration is calculated according to:

$$\text{Conc } (\mu\text{g}/\text{m}^3) = \text{Extract Conc } (\mu\text{g}/\text{mL}) \times 10 \text{ mL} / \text{Air Volume Sampled } (\text{m}^3)$$

## **6. QUALITY ASSURANCE**

### **A. Instrument Reproducibility**

The reproducibility of the instrument and analytical method was established by analyzing five (5) 1.0  $\mu\text{L}$  injections of propanil standard at three concentrations (low, mid, and high). The low, mid and high concentrations were 0.01, 0.1 and 0.2  $\mu\text{g}/\text{mL}$ , respectively for ambient and 0.4, 2.0, and 4.0  $\mu\text{g}/\text{mL}$  for application.

### **B. Calibration**

A daily five-point calibration curve is made ranging from 0.01-0.20  $\mu\text{g}/\text{mL}$  (ambient) and 0.40-4.0  $\mu\text{g}/\text{mL}$  (application).

### **C. Calibration Check**

A calibration check sample is run after the calibration, after every ten samples and at the end of the sample batch to verify the calibration. The value of the check must be within  $\pm 3\sigma$  (the standard deviation) or  $\pm 10\%$  of the expected value whichever is greater. If the calibration check is outside the limit, then those samples in the batch after this calibration check need to be reanalyzed.

### **D. Minimum Detection Limit**

The detection limit is based on US EPA MDL calculation. Using the analysis of seven (7) replicates of a low-level matrix spike, the method detection limit (MDL) and the estimated quantitation limit (EQL) for propanil is calculated by:  $\text{MDL} = 3.14 \times (\text{std dev values})$ , where std dev =

the standard deviation of the concentration calculated for the seven replicate spikes. For propanil the MDL is 0.019 µg/sample (0.0019 µg/mL). EQL, defined as 5\*MDL, is 0.095 µg/sample (0.0095 µg/mL) based on a 10.0 mL extraction volume. Results are reported to three significant figures. Results below EQL but above the MDL are reported to one significant figure. Results less than the MDL are reported as less than the value of the MDL to one significant figure.

#### E. Collection and Extraction Efficiency (Recovery)

Propanil at a low and high level are spiked on the filters (three at each concentration). The spiked filters are placed on field samplers with airflows of 3 LPM for 24 hours. The samples are extracted with DCM and prepared as described in section 5, #6-7. The average percent recovery of propanil should be  $\pm 20\%$  of the expected value. The recoveries both for the low and high levels are at or near 100%.

#### F. Storage Stability

Storage stability is set up for a four-week study and will run concurrent with the field analysis. Three (3) filters each are spiked at the low and high-end concentrations. The filters are stored in the refrigerator until analyzed.

#### G. Breakthrough

No breakthrough analysis study was conducted. Recovery of spiked filters is at 100%.

#### H. Safety

This procedure does not address all of the safety concerns associated with chemical analysis. It is the responsibility of the analyst to establish appropriate safety and health practices. For hazard information and guidance refer to the material safety data sheets (MSDS) of any chemicals used in this procedure.

**APPENDIX B:**  
**USE INFORMATION, APPLICATION MONITORING AND AMBIENT AIR MONITORING**  
**RECOMMENDATIONS FOR THE PESTICIDE ACTIVE INGREDIENT 3,4-**  
**DICHLOROPROPIONANILIDE (PROPANIL) AND BREAKDOWN PRODUCT 3,4-**  
**DICHLOROAINELINE**

[http://www.cdpr.ca.gov/docs/emon/pubs/tac/recomm/propanil\\_final.pdf](http://www.cdpr.ca.gov/docs/emon/pubs/tac/recomm/propanil_final.pdf)